Horizontal Growth of Oxide and Nitride Nanowires and Nanobelts and Their Assembly

In designing hierarchal assemblies of nanocrystals to nanodevices with sophisticated functions, the shape of the nanocrystal (building block) plays an important role in the overall architecture of the device. One-dimensional building blocks, e.g., nanowires are among the most attractive nanostructures due to their morphology and compatibility with the existing technologies. The most challenging part of a nanodevice fabrication is placing the nanowires (NWs) into their proper place. All current techniques used in the manipulation of nanowires require post-growth treatments. In our lab, we are able to eliminate many of the post-growth treatments while still controlling the precise location and placement of the nanowires. Currently, the attempt is to expand this capability to an industrial scale and to other nanomaterials.

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The research described in this report includes 1) controlled positioning of NWs and their assembly, 2) developing on-surface synthetic routes for preparation of two popular classes of oxide and nitride semiconductor NWs, 3) their structural characterization by electron backscatter diffraction (EBSD), energy dispersive x-ray analysis (EDX), atomic force microscopy (AFM) and scanning electron microscopy (SEM). In the case of oxide semiconductors, for the first time, we were able to grow horizontally oriented ZnO nanobelts (Figure 1a and 1b). Although this effect is still under study, results show that by increasing the ratio of oxygen to zinc atoms in the growth media nanobelts grow instead of NWs. The nanobelts have rectangular cross sections with only one dimension (height) less than 20 nm and their length up to 10 micrometers. Their growth direction is similar to the previously found growth direction in ZnO NWs. In sensing applications, nanobelts morphologically seem to be preferred rather than NWs due to their rectangular cross-section and more exposed surface area. In synthesis of other oxide semiconductors, for the first time, horizontally grown In_2O_3 nanobelts on Si(100) have been prepared (Figure 1c). We have found two distinct growth directions for these belts (Figure 1d, red arrows). In_2O_3 is known as a suitable material for chemical sensing and has been used as thin film or sintered particles in sensors. These new nanobelts, due to their unique growth directions could result in developing sensing elements with new architectures and more robust properties. EDX analysis of an individual nanobelt is shown in Figure (1e), in which the In Lα characteristic x-ray line can be distinguished from the background. Each nanobelt starts from a spherical particle, which is not the Au catalyst. The origin of this catalytic process is not known yet and more in-depth study is under way in collaboration with MSEL to understand this process.

Controlling the length and arrangement of NWs on a surface are two crucial factors in device assembly. The goal has been developing techniques for faster, reliable, and repeatable nanowire device fabrication with the increased understanding of parallel functioning of a large number of nanodevices. Employing ZnO NWs as the building block, we have shown that the length of nanowires can be extended up to 10 micrometers (Figure1f), something which was difficult to achieve in the past. It is noteworthy that the growth of NWs is very sensitive to the flow and ratio of the incoming gases and slight changes in the substrate position can result in a different NW length. The issue of length reproducibility is in final stages of study. With respect to the exact positioning of NWs, we have shown that NW location can be controlled with a very high precision using electron beam lithography (Figure 1f). This capability is under adaptation to photolithography for its ease of use and scalability.

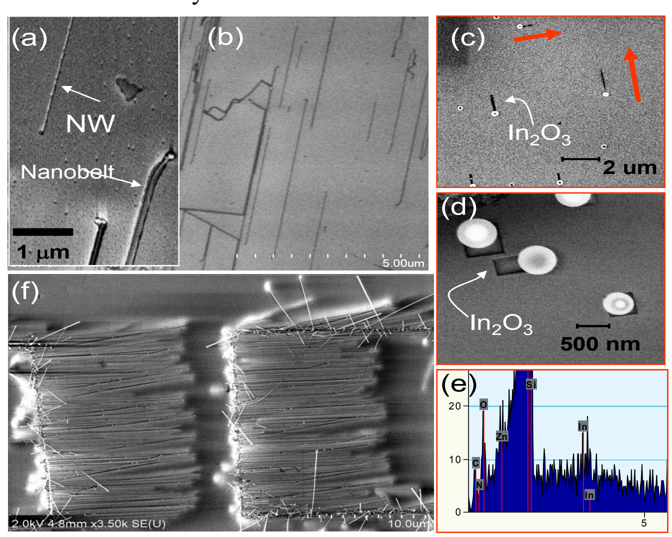

Fig. 1: *a, b) In an oxygen rich environment, horizontally grown ZnO nanobelts are grown instead of NWs the orientation of nanobelts can also be seen. c) In_2O_3 nanobelts grown on Si (001) surface show two perpendicular growth directions. d) A closer look at In_2O_3 nanobelts at early stage of growth. The growth starts where the large spheres are located. Based on EDX results (e), the spheres are either In or In_2O_3 . (Note that this process is not an Au catalyzed one). Very long ZnO NWs (f) are grown from Au lines with thickness of 10 nm and lateral dimension of 150 nm.*

Under certain conditions NWs tend to grow longer; this depends on the location of the substrate and ratio of zinc and oxygen atoms. Control over location and length are crucial factors in device fabrication.

The study of crystal structure of individual NWs has been studied using electron back-scattered diffraction (EBSD). Our results indicate that the majority of NWs have similar growth directions; an example is shown in Figure (2). In this figure, the growth direction of ZnO crystal is examined for several NWs grown from an Au pad on sapphire (Fig.2a). On the right side of this figure, individual NWs are shown in which the red marker indicates the spot that the back-scattered electrons were collected. The hexagons are generated from diffraction lines and represent the ZnO crystal axes. For NWs labled #1, 3, and 4, the gray hexagon indicates that the planes of zinc and oxygen atoms are parallel to the plane of the substrate, meaning direction normal to this plane is [001]. For NWs #2 and 5, the [001] direction is tilted 30º relative to the substrate plane, as shown in cartoon in the bottom left of Figure 2; these NWs appear to be an anomaly.

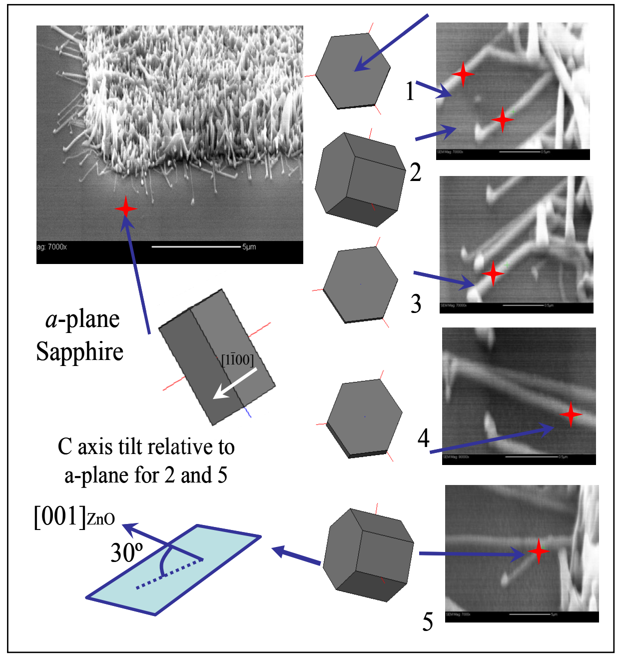

Fig. 2: *The top left of the figure shows NWs grown from a Au pad. These NWs are thicker in diameter and are used in EBSD experiments for obtaining stronger diffraction patterns. The long side of this figure is perpendicular to the growth direction of NWs. The right side of the figure illustrates NWs used in EBSD analyses. The hexagons show the ZnO crystal axes and the growth direction for NWs #1, 3, and 4.*

We have achieved two new milestones in two areas of nanomaterial preparation and nanomaterial assembly. The newly produced form of ZnO, i.e., *aligned nanobelts*, will be an attractive material in variety of applications spanning from crystal growth to sensors to light emitters. In assembly of nanowires, we were able to understand the main factors controlling the location and length of NWs. Earlier this year the significant potential impact of this work was recognized by the scientific community, as the highlights/vignettes have appeared on nearly a dozen nanotechnology-focused websites world-wide, ranging from “popular scientific magazines” (e.g., US Tech) to science “foundation” venues (e.g., The Foresight Institute). The dramatically reduced process time together with the inherent control of NW and nanobelt placement described in the paper in Applied Physics Letters should facilitate fabrication of nanoscale devices.

Future plans:
Science and technology at nanoscale are fast growing areas, and it is important to realize the potentially marketable sectors of these areas. To this end, NW based devices are promising candidates due to their easier incorporation into existing technology. Our main goal will be use of technologically relevant nanomaterials, developing measurement platforms and device fabrication protocols suitable for fulfilling growing demands in this area.

Reference:

B. Nikoobakht, C. A. Michaels, M. D. Vaudin, S. J. Stranick. “ **Horizontal Growth and *In Situ* Assembly of Oriented Zinc Oxide Nanowires.”** *Appl. Phys. Lett.* **2004**, 85(15), 3244.